sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities

total mass: ? g

dissolve in water, filter

insoluble impurities

mass: ? g

aq. sol'n of unk. sodium salt + sol. impurities
decolorize, filter

colored dye(s)
mass: ~ 20 mg

aq. sol'n of unk. sodium salt + sol. impurities

conc. HCl; filter

crude unk. carboxylic acid

mass: ? g

water-soluble imp.

Melting point ("mp")

Recrystallize

"pure" unk. carboxylic acid

mass: ? g

Identify unknown carboxylic acid

account for all masses; calculate % recovery

CH361/361H

Week 2 Lecture

End-point & Potentiometric Titrations
sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities

total mass: ? g

dissolve in water, filter

insoluble impurities
mass: ? g

daq. sol’n of unk. sodium salt + sol. impurities

decolorize, filter

colored dye(s)
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daq. sol’n of unk. sodium salt + sol. impurities

conc. HCl; filter

water-soluble imp.
crude unk. carboxylic acid
mass: ? g

melting point ("mp")

recrystallize

“pure” unk. carboxylic acid
mass: ? g

mp, MW, pK<sub>a</sub>, derivative mp

Identify unknown carboxylic acid

account for all masses; calculate %recovery
Recrystallization – practical considerations

Progressive approach:
1) solvent selection on micro-scale (~20 mg)
2) medium batch (~100 – 200 mg)
3) large batch (~3 – 5 g) – also involves hot filtration

Solvent selection
- sample must be completely **dry**!
- careful, detailed observations are crucial!
- begin with 20 mg in ~0.1 mL solvent; incrementally add more solvent
- if > 1.0 mL solvent required, solvent is not suitable

Solvent choices
- water
- ethanol (CH₃CH₂OH)
- hexane (CH₃CH₂CH₂CH₂CH₂CH₃)
- toluene (methylbenzene)

Mixed solvent systems
- water/ethanol
- hexane/toluene
Recrystallization – *practical considerations*

Common “pitfalls”:

1) crystals do not form
   - *seed crystal*
   - “scratching”
   - too much solvent?

2) crystals are of insufficient purity
   - *was solution cooled slowly?*
   - *inappropriate solvent*
   - *sample “melting” at boiling point of recrystallization solvent*

3) low recovery
   - *filtrate (mother liquor) contains compound of interest*
   - too much solvent?
   - insufficient cooling
Recrystallization

Crystallization that occurs with slow cooling:

Crystallization that occurs with fast cooling:

Images downloaded from:
http://orgchem.colorado.edu/Technique/Procedures/Crystallization/Crystallization.html
sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities

total mass: ? g

dissolve in water, filter

insoluble impurities

mass: ? g

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crude unk. carboxylic acid

mass: ? g

water-soluble imp.

recrystallize “pure” unk. carboxylic acid

mass: ? g

mp, MW, pK_a, derivative mp

Identify unknown carboxylic acid

account for all masses; calculate %recovery

mp = 148 °C

mp = 143-145 °C

C_7H_4Cl_2O_2

mol. wt. = 191.01

C_7H_5BrO_2

mol. wt. = 201.02

pK_a = 2.85

pK_a = 1.82

melting point (“mp”)
sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities

total mass: ? g

dissolve in water, filter

insoluble impurities mass: ? g

aq. sol'n of unk. sodium salt + sol. impurities
decolorize, filter colored dye(s)
mass: ~ 20 mg

aq. sol'n of unk. sodium salt + sol. impurities
conc. HCl; filter crude unk. carboxylic acid
mass: ? g

water-soluble imp.
recrystallize "pure" unk. carboxylic acid
mass: ? g

Identify unknown carboxylic acid

mp, MW, pK\textsubscript{a}, derivative mp

"pure" unk. carboxylic acid

mass: ? g

melting point ("mp")

Identify unknown carboxylic acid

account for all masses; calculate %recovery

mp = 148 °C

mp = 143-145 °C

C\textsubscript{7}H\textsubscript{5}BrO\textsubscript{2}

mol. wt. = 201.02

C\textsubscript{7}H\textsubscript{4}Cl\textsubscript{2}O\textsubscript{2}

mol. wt. = 191.01

pK\textsubscript{a} = 2.85

pK\textsubscript{a} = 1.82
sodium salt of unknown aromatic carboxylic acid + soluble impurities + insoluble impurities
total mass: \(? \text{ g}\)

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decolorize, filter

colored dye(s)
mass: \(~20 \text{ mg}\)

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recrystallize "pure" unk. carboxylic acid
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Identify unknown carboxylic acid

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mp, MW, pKₐ, derivative mp

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C₇H₅BrO₂
mol. wt. = 201.02
pKₐ = 2.85

mp = 143-145 °C
C₇H₄Cl₂O₂
mol. wt. = 191.01
pKₐ = 1.82

melting point ("mp")
Titration

Method to determine the concentration of an analyte, through the slow, incremental addition of a known concentration of another reagent

Acid-Base Titration:

\[
\text{NaOH} \quad \{ \quad \text{ArCOOH} \quad \}
\]

\[
\text{Ar-C-O-H} + \quad \text{OH}^{-} \quad \rightarrow \quad \text{Ar-C-O}^{-} + \quad \text{H}_2\text{O}
\]

unknown acid (weak) hydroxide (strong base) conjugate base conjugate acid

Determining the Equivalence Point:

- pH vs. vol. NaOH added (potentiometric)
- Color change of pH indicator (end-point)

End-Point Titration

- Data allows calculation of equivalent weight of unknown acid
  
  *(for a monoprotic acid, equivalent weight = molecular weight)*

- Phenolphthalein is the end-point indicator you will use
  
  **unless you are colorblind to red**
  
  *(if so, inquire about alternative indicators)*

---

**Figure from “Principles of Chemistry: A Molecular Approach, 2nd Edition” by N. Tro (Pearson)**
End-Point Titration: Practical Considerations

Titrations must be carried out carefully!

- obtain accurate mass of unknown
- acid must be completely dissolved
  (~0.3 g/50 mL; can add some ethanol if needed)
- proper buret reading
- may need to add fraction of a drop of NaOH solution
- must obtain 2 measurements within 0.5% of each other
- do not “overshoot” the end-point

- make all measurements to 4 significant figures

End-Point Titration: **Practical Considerations**

*Example calculation and consequences of errors*

- **254.2 mg** of dry purified acid titrated with **0.1033 N** aq. NaOH

  > end-point reached upon addn. of **12.24 mL** of base

  > # mmols of base = 0.1033 mmol mL\(^{-1}\) x 12.24 mL
  
  > = 1.264 mmol

  > mol. wt. of acid = 254.2 mg / 1.264 mmol
  
  > = 201.11 g mol\(^{-1}\)

**Example calculation and consequences of errors**

\[
\begin{align*}
\text{mp} & = 148 \, ^\circ\text{C} \\
\text{mol. wt.} & = 201.02 \\
\text{mp} & = 143-145 \, ^\circ\text{C} \\
\text{mol. wt.} & = 191.01
\end{align*}
\]
End-Point Titration: Practical Considerations

Example calculation and consequences of errors

- **254.2 mg** of dry purified acid titrated with **0.1033 N** aq. NaOH

  - end-point reached upon addition of **12.24 mL** of base
  - # mmols of base = \(0.1033 \text{ mmol mL}^{-1} \times 12.24 \text{ mL}\)
    - \(= 1.264 \text{ mmol}\)
  - mol. wt. of acid = \(254.2 \text{ mg} / 1.264 \text{ mmol}\)
    - \(= 201.11 \text{ g mol}^{-1}\)

BUT, what if acid was not dry?

  - e.g., only 95 wt.% pure

true mol. wt. of acid = \(241.5 \text{ mg} / 1.264 \text{ mmol}\)
  - \(= 191.05 \text{ g mol}^{-1}\)

\[
\begin{align*}
\text{mp} &= 148 ^\circ \text{C} \\
\text{C}_7\text{H}_5\text{BrO}_2 &\quad \text{mol. wt.} = 201.02 \\
\text{mp} &= 143-145 ^\circ \text{C} \\
\text{C}_7\text{H}_4\text{Cl}_2\text{O}_2 &\quad \text{mol. wt.} = 191.01
\end{align*}
\]
End-Point Titration: *Practical Considerations*

*Example calculation and consequences of errors*

- **254.2 mg** of dry purified acid titrated with **0.1033 N aq. NaOH**
  - end-point reached upon addition of **12.24 mL** of base
  - # mmols of base = 0.1033 mmol mL\(^{-1}\) × 12.24 mL
    - = **1.264 mmol**
  - mol. wt. of acid = 254.2 mg / 1.264 mmol
    - = **201.11 g mol\(^{-1}\)**

**BUT, what if we over shot end-point?**
- e.g., true value 12.00 mL
  - true mol. wt. of acid = 254.2 mg / 1.240 mmol
    - = **205.00 g mol\(^{-1}\)**
Potentiometric Titration

- Data allows determination of pK\(_a\) of unknown acid

\[
\text{Ar–C–O–H} + \text{H}_2\text{O} \rightleftharpoons \text{Ar–C–O}\,^- + \text{H}_3\text{O}^+
\]

\[
K_a = \frac{[\text{ArCOO}^-][\text{H}_3\text{O}^+]}{[\text{ArCOOH}]} \\
pK_a = -\log(K_a)
\]

- As hydroxide is added, a buffer system develops

\[
\text{Ar–C–O–H} + \,^-\text{OH} \rightarrow \text{Ar–C–O}\,^- + \text{H}_2\text{O}
\]

\[
pH = pK_a + \log \left( \frac{[\text{ArCOO}^-]}{[\text{ArCOOH}]} \right)
\]

- When [ArCOO\(^-\)] = [ArCOOH], pH is equal to the pK\(_a\) of the unknown acid
Potentiometric Titration

Figure downloaded from UC Davis ChemWiki website
Potentiometric Titration: *Practical Considerations*

- prepare a solution of ~100 mg in 100-150 mL
- acid must be completely dissolved
  (ethanol will obscure results – use only if needed)
- heat solution to aid dissolution
  *do not begin titration until solution has cooled to 25°C*
- interpret $pK_a$ data with caution

![Chemical Structures]

- mp = 148 °C  
  $C_7H_5BrO_2$  
  mol. wt. = 201.02  
  $pK_a = 2.85$

- mp = 143-145 °C  
  $C_7H_4Cl_2O_2$  
  mol. wt. = 191.01  
  $pK_a = 1.82$
Tasks for Week 2: Trial, Medium, and Large Batch Recrystallizations

- polar non-ionic compound
- sparing solubility in H₂O

precipitate (solid) + related impurities

Wednesday
- conclude trial recrystallizations and apply selected solvent to medium batch – check % recovery, if ca. ≥75%, solvent system OK for large batch (rest of material)

Wed./ Fri.
- large batch recrystallization, collect and dry material (oven), need ca. 4 g (after drying to constant weight), accurately determine melting point of pure acid

(Friday)
- TIME ALLOWING – begin end-point titrations

crude unk. carboxylic acid
mass: ? g

recrystallize

“pure” unk. carboxylic acid
mass: ? g

mp, MW, pKₐ, derivative mp

melting point (“mp”)